

Review of Recent Publications Relating to the Ozone Weekend Effect in California

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Executive Summary

The occurrence of higher ozone concentrations on weekends than on weekdays in some areas has come to be known as the weekend effect. Because emissions of ozone precursors - nitrogen oxides (NO_x) and volatile organic compounds (VOC) - are generally expected to be lower on weekends than on weekdays, the weekend effect is counterintuitive and may have implications for ozone control strategies.

Recent studies all concur in concluding that a weekend effect occurs in California throughout much of the South Coast Air Basin (SoCAB), the San Francisco Bay Area, and the San Diego metropolitan area; it also occurs at monitoring sites within other urban centers, including Sacramento, Stockton, and Fresno (Austin et al., 2000; Blanchard and Tanenbaum, 2000; Fujita et al, 2000; Altshuler et al., 1995).

These same studies also consistently concur in concluding that ambient concentrations of ozone precursors are lower during the daytime on weekends than on weekdays throughout most of eight air basins in California (San Francisco Bay area, Sacramento Valley, San Joaquin Valley, South Coast, South Central Coast, San Diego, Mojave Desert, and Salton Sea). The magnitudes of the differences vary from hour to hour, but at most monitoring sites the weekend levels appear to average approximately 10 to 40 percent lower between sunrise and the peak ozone hours. NO_x concentrations are reduced more than VOC concentrations on weekends.

Of six candidate proposed explanations of the weekend effect, a recent CARB report (Austin et al., 2000) concluded that presently available data were sufficient to show that two were not plausible. The two implausible hypotheses were "carryover near the ground" and "increased weekend emissions", both of which are refuted by ambient measurements showing lower concentrations of ozone precursors during daytime weekend hours than during corresponding weekday hours. Three hypotheses were considered plausible, but not proven: "NO_x reduction", "NO_x timing", and "carryover aloft." Each of these three hypotheses involves the complex role of NO_x as a precursor for ozone, and they are not

mutually exclusive. Finally, a "soot and sunlight" hypothesis was considered theoretically plausible, but lacking in either supporting or refuting data.

A key commonality of the three plausible hypotheses with supporting data is that all involve the effects of NO_x on ozone; the hypotheses are in fact tightly linked. They differ in the degree of emphasis placed on the effects of mid-day emissions of NO_x , and the relative contributions of carryover ozone to peak ozone concentrations. Review of the full range of available studies, including Austin et al. (2000), Fujita et al. (2000), Blanchard and Fairley (1999), and Blanchard and Tanenbaum (2000), shows that all concur in describing the effects of lowered NO_x levels on ozone formation at urban-center sites: NO concentrations fall to low levels earlier, and ozone formation begins earlier, on weekends than on weekdays at sites in the South Coast Air Basin (Fujita et al., 2000); "Ozone concentrations at many sites (not including far downwind sites) tend to increase earlier in the day on weekends compared to weekdays." (Austin et al., 2000). These effects are expected, based upon a large body of historical work, at locations where ozone formation is radical (VOC)-limited: fresh NO emissions lower ozone concentrations by virtue of the reaction of NO with ozone, and they reduce rates of ozone formation by lowering radical concentrations.

Substantial agreement also exists among both the recent studies and historical work (see e.g., Chameides et al., 2000) in identifying where ozone formation is limited by radicals (VOC) and where it is limited by NO_x in California. The CARB report (Austin et al., 2000) found that daytime surface VOC/NO_x ratios indicate that ozone formation in most of the South Coast Air Basin is VOC-limited, with some uncertainty stemming from possible measurement biases. Past modeling studies and analyses of ambient measurements have both shown that ozone formation in the western and central portions of the South Coast Air Basin (Los Angeles and Orange counties) is VOC-limited, while in the eastern basin (i.e., Chino to Riverside to Banning), ozone formation is either NO_x -limited, or peak ozone concentrations could be lowered by reductions of either VOC or NO_x (Chameides et al., 2000). And Blanchard and Fairley (1999) and Blanchard and Tanenbaum (2000) show that the spatial patterns of the weekend effect match the spatial patterns delineating where ozone formation is VOC limited in both southern and northern California: the weekend effect occurs at locations where ozone formation is

VOC-limited.

In California, the full range of situations identified in the recent NARSTO ozone assessment report (Chameides et al., 2000) exists, each of which may require a different ozone management strategy. The spatial variations of the weekend effect appear to be one indication of this variety. Regardless of the relative contributions of each plausible process to the overall weekend effect, ample scientific evidence exists to indicate that the range of conditions in California requires geographically-focused reductions of VOC and NO_x emissions, with emphasis on VOC reductions in areas known to be strongly VOC-limited (e.g., most of the San Francisco Bay Area, South Coast Air Basin, and San Diego Air Basin) and NO_x reductions where ozone is NO_x-limited. The latter involve regional ozone reductions, and require statewide control strategies in some cases (e.g., motor vehicles). The weekend effect indicates that careful consideration should be given to the balance of VOC and NO_x controls imposed within the coastal metropolitan areas. The undisputed magnitudes of the increased weekend ozone concentrations within the San Francisco Bay Area, South Coast Air Basin, San Diego Air Basin, and some urban locations within the Central Valley indicate that control strategies in which NO_x emission reductions exceed VOC emission reductions are likely to aggravate ozone concentrations in those areas. The weekend effect provides a clear test case.

Emission-control strategies that most rapidly reduce ozone concentrations within the Bay Area and the SoCAB should also benefit downwind areas by reducing the levels of transported ozone. NO_x reductions within NO_x-limited areas, such as east of Sacramento, should be effective in reducing ozone concentrations in those areas; NO_x reductions made upwind in VOC-limited areas may not reduce ozone formation downwind, and may lessen progress in reducing downwind ozone concentrations by slowing rates of ozone reductions in the upwind areas. These observations should be tested using three-dimensional model studies with appropriate databases and model evaluation.

Ongoing field studies are already in place to provide further data for understanding the weekend effect (Fujita et al., 2000). The need for an additional comprehensive and extended field program to

further distinguish among the plausible explanations of the weekend effect is not apparent. A more productive use of resources would be to focus on evaluating geographically-targeted ozone control strategies, rather than on testing hypotheses of the weekend effect. Further analysis of data from the 1997 Southern California Ozone Study (SCOS97) and the ongoing Central California Ozone Study (CCOS) projects, along with modeling studies, should be pursued. An additional topic meriting further investigation is the effect of VOC and NO_x reductions on aerosol nitrate formation. Existing studies indicate that aerosol ammonium-nitrate formation in California is typically not limited by the availability of ammonia. However, existing work from the San Joaquin Valley Integrated Monitoring Study of 1995 (IMS95) also suggests that VOC reductions may reduce the rate of aerosol nitrate formation more effectively than NO_x reductions in areas where ozone formation is VOC limited. This topic should be investigated through analyses of data from the Central California Regional Particulate Air Quality Study (CRPAQS), along with modeling studies.

Introduction

The occurrence of higher ozone concentrations on weekends than on weekdays in some areas has come to be known as the weekend effect. Because emissions of ozone precursors - nitrogen oxides (NO_x) and volatile organic compounds (VOC) - are generally expected to be lower on weekends than on weekdays, the weekend effect is counterintuitive and may have implications for ozone control strategies.

Several recently completed or ongoing studies have dealt with the weekend effect in California. They include a draft staff report by the California Air Resources Board (CARB) (Austin et al., 2000), analyses of ambient monitoring data (Blanchard and Tanenbaum, 2000; Fujita et al, 2000), an ongoing air quality modeling study (Yarwood, 2000), and an ongoing field program (Fujita et al, 2000). Other ongoing studies are examining the weekend effect in locations outside California (Pun and Seigneur, 2000).

While there has been considerable recent interest in the weekend effect, the occurrence of higher ozone concentrations on weekends than on weekdays has in fact been noted for many years and in a variety of locations (Cleveland et al., 1974; Lebron, 1975; Graedel et al., 1977; Elkus and Wilson, 1977; Hoggan et al., 1989; Altshuler et al., 1995). Not all areas exhibit higher ozone levels on weekends than on weekdays, though (Rao et al., 1991).

In this report, we review the recent studies of the weekend effect in California, with reference to the larger body of literature. The conclusions and recommendations of the CARB report are considered in relation to the findings of other studies. The studies of the weekend effect in California are also reviewed in relation to the recently completed NARSTO ozone assessment document (Chameides et al., 2000).

Where and When Does the Weekend Effect Occur?

The recent California studies are very consistent in identifying where the weekend effect occurs:

primarily in metropolitan areas located near the coast. According to the CARB report,

"The ozone weekend effect occurs at most, if not all, of the monitoring sites in the Los Angeles and San Francisco metropolitan areas, based on measurements during the ozone seasons of 1996 through 1998. However, the ozone weekend effect is absent or negligible at most sites in the Sacramento and San Joaquin Valleys."

A variety of studies of the weekend effect in the South Coast Air Basin, summarized by Fujita et al. (2000), show that,

"The distribution by day-of-the-week of the ten highest ozone concentrations in the Basin for each year for each station in the period 1986-93, showed these episodes occurred significantly more often on Saturdays than on Sundays through Wednesdays... During 1992-94, the typical pattern for ozone in many sites in Los Angeles is a large increase from Friday to Saturday, no change or a slight decrease from Saturday to Sunday, then a large decrease from Sunday to Monday."

Blanchard and Fairley (1999) concluded that,

"For the Bay Area, eleven sites show significant weekend effects (two-sided p-values < .05) and no site shows a *weekday* effect. In fact, the weekend mean exceeded the weekday mean at every Bay Area site. For the Sacramento Valley, the weekday mean is higher than the weekend mean at every site, and this weekday effect is statistically significant at six sites. For the San Joaquin Valley, effects are mixed: no site shows a statistically significant *weekend* effect, while three show a significant *weekday* effect. Weekend means were lower than weekday means at most sites in the Sierra Nevada, while the reverse was true for many urban locations (Fresno area, Stockton, Modesto)."

Blanchard and Tanenbaum (2000) found that,

"Peak ozone values were higher on weekends than on weekdays at many sites in the South Coast and San Diego air basins. The effect was reversed at many sites in the Mojave and Salton Sea air basins. Weekend-weekday ozone differences during the periods 1991 through 1994 and 1996 through 1998 were similar to those for the full period from 1991 through 1998."

The maps prepared by Blanchard and Fairley (1999) and Blanchard and Tanenbaum (2000) provide convenient summaries of the weekend effect (Figures 1 and 2).

In the South Coast Air Basin, the weekend effect has become more pronounced over time. Fujita et al. (2000) found that the weekend effect was weak during the 1980s; indeed, in most of the central and eastern portions of the basin, ozone levels were higher on weekdays during the years 1981-84, and weekends and weekdays were not statistically different between 1985 and 1989. The CARB report (Austin et al., 2000) also found that the weekend effect became more pronounced over time, with average Sunday ozone levels shifting from less than Saturday levels in the early 1990s to greater than Saturday levels in the late 1990s in the South Coast Air Basin, the San Francisco Bay Area, and the Sacramento Area.

According to the CARB report, from 1996 through 1998, weekend ozone levels weekends were typically 22 ppbv (32 percent) higher than on Fridays in the South Coast Air Basin and 9 ppbv (25 percent) higher than on Fridays in the San Francisco Bay Area. Fujita et al. (2000) reported an average increase of 26 percent from Wednesday to Sunday at sites in the South Coast Air Basin during the years 1995 through 1998. A weekend effect of 10 to 20 ppbv may pose significant difficulties for locations attempting to meet the 1-hour California ozone standard (90 ppbv) or the proposed federal 8-hour ozone standard (80 ppbv). However, most sites in the San Francisco Bay Area currently meet the 1-hour federal ozone standard (120 ppbv).

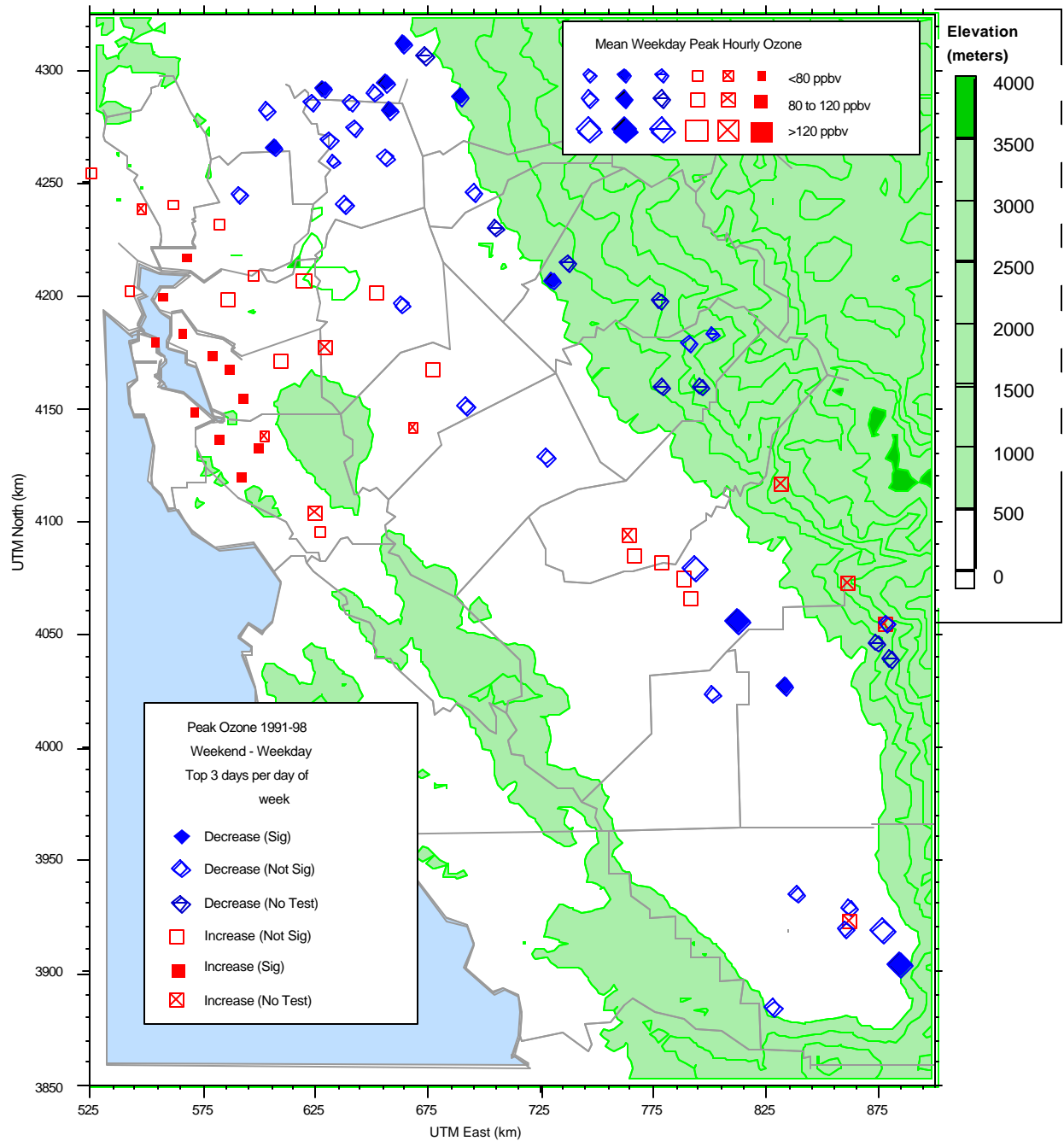


Figure 1. Comparison of mean weekend peak hourly ozone to mean weekday ozone levels at sites in central California. Sites marked as increasing had higher mean weekend values. Source: Blanchard and Fairley (1999).

Why Does the Weekend Effect Occur?

The CARB report identifies six hypotheses for study. These hypotheses were reviewed both internally and externally and refined at the beginning of the CARB study, and therefore represent a set of possible explanations that were considered plausible a priori by a reasonably broad section of the scientific community. The six hypotheses are (following CARB nomenclature):

- NO_x reduction
- NO_x timing
- Carryover near the ground
- Carryover aloft
- Increased weekend emissions
- Soot and sunlight

Of these six hypotheses, the CARB report concluded that presently available data were sufficient to show that two were not plausible. The two implausible hypotheses were "carryover near the ground" and "increased weekend emissions." The evidence refuting those two hypotheses will be summarized briefly below. Three hypotheses were considered plausible, but not proven: "NO_x reduction", "NO_x timing", and "carryover aloft." As will be discussed below, each of these three hypotheses involves the complex role of NO_x as a precursor for ozone, and they are not mutually exclusive. Finally, the "soot and sunlight" hypothesis was considered theoretically plausible, but lacking in either supporting or refuting data.

Not an Explanation - Increased Emissions or Carryover Near the Ground. The "increased emissions" hypothesis assumes that weekend emission levels are greater than weekday levels. "Carryover near the ground" assumes that traffic volumes on Friday and Saturday nights are greater than other evenings, and provide a larger reservoir of ozone precursors that then initiate higher rates of ozone formation on Saturday and Sunday mornings. Both these hypotheses have been disproved by straightforward analyses of ambient concentrations of NO_x, VOC, VOC species, and CO, which show

that daytime levels of all precursors are lower on weekends than on weekdays. As discussed below, concentrations of some species are indeed higher between about 10 pm and 4 am on Friday and Saturday evenings than on other nights, but these higher levels do not persist into the day. The amounts of precursors added beginning by about 5 am on weekdays quickly raise weekday precursor concentrations above the weekend levels.

All studies concur that ambient concentrations of ozone precursors are, for the most part, lower on weekends than on weekdays. The CARB report (Austin et al., 2000) concluded,

"Extra traffic on Friday and Saturday nights may inject additional ozone precursors into the air at the surface, but air quality data do not indicate a significant impact of these emissions on ozone formation the following day ... Measured concentrations of CO, VOC's and NO_x at sunrise on Saturday and Sunday mornings are lower than the corresponding weekday concentrations. Therefore, ozone precursors that carryover under the surface-based inversion on Friday and Saturday nights do not appear to be a significant cause of the ozone weekend effect."

The CARB report also concluded that,

"With the exception of Saturday afternoon, concentrations of CO and NO_x tend to be lower on weekends compared to weekdays."

Fujita et al. (2000) reported that in the South Coast Air Basin,

"Average 7-8 a.m. NO concentrations on Saturday and Sunday are 55-70 percent and 33-39 percent of the average weekday concentrations, respectively ... Average 7-8 a.m. CO and NMHC (estimated from CO) on Saturday and Sunday are 67-83 percent and 50-65 percent of the average weekday concentrations, respectively."

Blanchard and Fairley (1999) concluded that in northern and central California,

"Weekend NO_x levels averaged 27 percent lower than weekday levels at the time of the peak ozone hour ... The weekend NO_x means at other times averaged 23 to 40 percent lower than the weekday means ... Weekend means for hourly NMHC and multi-hour total NMOC and gas-phase organic compounds were generally lower than weekday means ... Averaged over sites, the weekend means for organic compounds were 5 to 25 percent lower than weekday

means ...”.

Blanchard and Tanenbaum (2000) concluded that in southern California,

"Throughout the entire five-basin study domain, daytime ambient concentrations of ozone precursors were lower on Saturdays and Sundays than on weekdays, though not all differences were statistically significant at all monitoring sites. The evidence for lower NO_x was stronger than the evidence for lower NMOC. ... On Saturdays, daytime concentrations of NMOC, NMHC, and NO_x were about 10 to 20 percent lower than on weekdays, averaging weekday-Saturday differences across all sites. On Sundays, NMOC, NMHC, and NO_x averaged about 15 to 40 percent lower than on weekdays, again averaging weekday-Sunday differences across sites.”

Empirical evidence therefore consistently demonstrates that ambient concentrations of ozone precursors are lower during the daytime on weekends than on weekdays throughout most of eight air basins in California (San Francisco Bay area, Sacramento Valley, San Joaquin Valley, South Coast, South Central Coast, San Diego, Mojave Desert, and Salton Sea). In summary, the magnitudes of the differences vary from hour to hour, but at most sites the weekend levels appear to average approximately 10 to 40 percent lower between sunrise and the peak ozone hours. NO_x concentrations are reduced more than VOC concentrations on weekends.

A Theoretical Explanation Lacking Evidence Pro or Con - Soot and Sunlight. The "soot and sunlight" hypothesis assumes that soot levels are lower on weekends than on weekdays, thus absorbing less ultra-violet (UV) radiation. UV radiation initiates and sustains the radical-propagating reactions that drive ozone production, so higher UV levels, in theory, would permit faster rates of ozone accumulation. The CARB report concludes that the "soot and sunlight" hypothesis is theoretically plausible, but available measurements are too limited to refute or support it. Analyses of ambient measurements do show that concentrations of particulate matter peak late in the workweek and are usually lower on Sundays than on other days (Austin et al, 2000), but these analyses have been carried out only for sites in the South Coast Air Basin and the majority of the differences were not statistically significant (Tran,

1999). Levels of particulate matter averaged approximately 10 to 30 percent lower on Sundays than on weekdays (Tran, 1999). However, no data were available to show whether or not any differences occurred between the weekday and weekend levels of UV radiation (specifically, in the "actinic flux", which is a measure of UV radiation that specifically relates to the photochemical reactions that drive ozone formation).

Recommendations in the CARB report include steps for acquiring data that would permit further evaluation of the "soot and sunlight" hypothesis. However, the need for such an evaluation should not be overrated. As discussed below, existing data already support three other hypotheses considered plausible by the CARB report - thus, measurements now indicate that the "soot and sunlight" hypothesis cannot be the only cause of the weekend effect.

The CARB report also notes that aerosol nitrate, derived from NO_x , can constitute a substantial portion of fine particulate mass. However, during warmer months when ozone concentrations reach high values, aerosol nitrate concentrations are low at most locations; conversely, aerosol nitrate concentrations are highest during winter months, when ozone concentrations are lowest. The temperature dependence of aerosol nitrate is related to an equilibrium reaction between aerosol nitrate and its gas-phase precursors, nitric acid and ammonia, which favors the gas-phase species as temperatures increase. Thus, aerosol nitrate is generally not a significant component of the aerosol mass during the time periods of interest for understanding the ozone weekend effect. However, aerosol nitrate formation is affected by both VOC and NO_x emission levels, as discussed later. Therefore, both ozone and aerosol formation need to be addressed in considering emission control strategies.

The Plausible Hypotheses Supported by Data. The three plausible hypotheses that are supported by measurements all involve NO_x . These three hypotheses are " NO_x reduction", " NO_x timing", and carryover aloft.

The " NO_x reduction" hypothesis is based on well-known aspects of ozone formation and

explains the weekend effect as an increase in ozone formation rates in response to lower NO_x levels at radical (VOC)-limited locations; in contrast, NO_x-limited locations may show a decrease in peak ozone levels in response to lower NO_x levels on weekends. A considerable body of research, including theory, environmental-chamber experiments, modeling, and analyses of ambient data, has shown that reductions of ambient NO_x levels can increase the rate of ozone formation which, under some circumstances, can cause increases in peak ozone concentrations. Increases in peak concentrations are likely when the rate of ozone formation is limited by the availability of radical species, rather than NO_x; decreases in peak concentrations are likely when peak values are limited by the availability of NO_x.

The "NO_x-timing" hypothesis, according to the CARB report, "assumes that NO_x emissions for several hours following sunrise are much lower on weekends (less commute traffic, etc.) compared to weekdays but increase substantially around mid-day. Because less NO_x is present to depress the concentration of radicals, the photochemical system becomes more active earlier in the day. As activities and emissions increase toward mid-day, the fresh NO_x enters this more active system, participates in ozone-generating reactions more efficiently, and leads to higher weekend ozone compared to weekdays."

The "Carryover aloft" hypothesis assumes that a reservoir of pollutants exists above the nocturnal boundary layer. "On weekdays, large amounts of fresh NO_x emissions titrate or "quench" the ozone and radicals so they have little effect on surface concentrations. On Saturday and Sunday, however, NO_x emissions are reduced substantially, ozone and radicals that carry over are not quenched, and they cause ozone measurements at the surface to be higher on weekends compared to weekdays."

In these statements of the three hypotheses, a key commonality is that all three involve the effects of NO_x on ozone: in each case, fresh NO emissions lower ozone concentrations by virtue of the reaction of NO with ozone, and they reduce rates of ozone formation by lowering radical concentrations. These hypotheses are therefore tightly linked, and are not mutually exclusive. They

differ in the degree of emphasis placed on the effects of mid-day emissions of NO_x , and the relative contributions of carryover ozone to peak ozone concentrations. The hypotheses were formulated as distinct explanations, because the CARB report argues that the NO_x -reduction and NO_x timing hypotheses "have substantially different policy implications with respect to NO_x controls as an ozone control measure." Similarly, in situations where there may be substantial contributions of carryover ozone to peak values, control strategies may differ from those used where little carryover occurs.

Control implications are discussed later in this report, where it will be proposed that in fact the same emission control implications derive from each hypothesis. Here, we summarize the evidence found for the roles of NO_x reduction, NO_x timing, and carryover aloft, keeping the scientific questions distinct from issues of ozone management.

NO_x plays a complex role in ozone chemistry. While lowering NO_x levels can, as noted, increase the rate of ozone formation, the same reduction also lowers the maximum amount of ozone that potentially can be produced given sufficient UV radiation. Over 90 percent of NO_x is emitted as NO, which reacts with ozone to generate NO_2 , thus initially decreasing ozone concentrations. However, NO_2 then initiates one or more cycles of reactions that result in further ozone production. Therefore, NO_x both promotes and inhibits ozone formation. The inhibition has two aspects. The first is the direct reaction of ozone with NO, already noted, which delays the onset of ozone formation until the bulk of the fresh NO emissions have been converted to NO_2 . The second aspect concerns the rate at which ozone can be produced. During the initial phases of ozone production (typically, morning hours), the rate of ozone formation depends upon ambient concentrations of radical species, particularly hydroxyl (OH) and peroxy (OH_2) radicals. These species react with hydrocarbon compounds to generate yet more radicals, a process that accelerates the rate of ozone formation. In a competing reaction, however, NO_2 reacts with OH to yield nitric acid (HNO_3), removing both NO_2 and OH from the cycle of ozone-producing reactions. So, raising the concentrations of NO_2 can reduce radical concentrations, in turn reducing the rate of ozone production. In contrast, lowering concentrations of NO_2 can increase radical concentrations, in turn increasing the rate of ozone production.

Substantial agreement exists among both recent and historical work in identifying where ozone formation is limited by radicals (VOC) and where it is limited by NO_x in California. For example, modeling studies and analyses of ambient measurements have both shown that ozone formation in the western and central portions of the South Coast Air Basin (Los Angeles and Orange counties) is VOC-limited, while in the eastern basin (i.e., Chino to Riverside to Banning), ozone formation is either NO_x -limited, or peak ozone concentrations could be lowered by reductions of either VOC or NO_x (Chameides et al., 2000). The CARB report (Austin et al., 2000) found that daytime surface VOC/ NO_x ratios indicate that ozone formation in most of the South Coast Air Basin is VOC-limited, with some uncertainty stemming from possible measurement biases. Modeling studies have also indicated that ozone formation in the San Francisco Bay Area and the northern San Joaquin Valley, including, e.g., Stockton and Modesto, is VOC limited; elsewhere in central California, ozone formation tends to be NO_x limited. These modeling studies are supported by analyses of ambient data (Blanchard, 1996). The data analyses by Blanchard and Fairley (1999) and Blanchard and Tanenbaum (2000) show that the spatial patterns of the weekend effect (Figures 1 and 2) match the spatial patterns delineating where ozone formation is VOC limited in both southern and northern California.

The studies also concur in describing the effects of lowered NO_x levels on ozone formation at urban-center sites. Fujita et al. (2000) showed that NO concentrations fall to low levels earlier, and ozone formation begins earlier, on weekends than on weekdays at sites in the South Coast Air Basin. The CARB report concurs: "Ozone concentrations at many sites (not including far downwind sites) tend to increase earlier in the day on weekends compared to weekdays." Blanchard and Fairley (1999) similarly show that ozone formation begins earlier on weekends than on weekdays at sites in the San Francisco Bay Area, thus allowing weekend peak ozone levels to reach higher values by midday. Moreover, the rates of ozone formation tend to be greater on weekends than on weekdays at many sites. Fujita et al. (2000) showed that of the 13 sites in the South Coast Air Basin with suitable data during the period 1995 through 1998, all showed an earlier start time for ozone formation on Sundays compared with Wednesdays (by ~0.5 to 2.5 hours); peak hours were unchanged. Nine showed a

higher rate of ozone accumulation on Sundays; at five, the Sunday rate was at least 2 ppbv hr⁻¹ greater than the weekday rate.

The same evidence supports the initial premise of the NO_x-timing hypothesis, but evidence for its second premise is lacking:

"Because less NO_x is present to depress the concentration of radicals, the photochemical system becomes more active earlier in the day. As activities and emissions increase toward mid-day, the fresh NO_x enters this more active system, participates in ozone-generating reactions more efficiently, and leads to higher weekend ozone compared to weekdays."

As found by all studies and noted above, the photochemical system does become active earlier on weekends. However, the rates of accumulation of ozone do not accelerate during the middle of the day at sites showing a weekend effect. Although Fujita et al. (2000) showed that 9 of the 13 sites in the South Coast Air Basin showed a higher rate of higher rate of ozone accumulation on Sundays during the period 1995 through 1998, no sites showed an acceleration of ozone formation just prior to the time of occurrence of the peak ozone concentration. Moreover, diurnal profiles show that the differences between weekend and weekday ozone concentrations begin early, with the earlier weekend "starting" time for ozone formation (when O₃ and NO concentrations become equal), and continue throughout the morning; the weekend effect does not occur as a sudden acceleration of ozone production at mid-day (see Figures 3 through 5 for examples). However, in some locations the data are not inconsistent with a small mid-day effect coinciding with the apparent input of fresh emissions, but this effect is modest in comparison with the differences between weekday and weekend ozone concentrations that can be traced through to earlier in the morning.

Diurnal concentration profiles also show that ambient CO and NO_x concentrations after about 4 a.m. on weekends are reasonably parallel with weekday concentrations. Some differences do occur, perhaps suggesting more sustained weekend emissions levels between about 8 and 10 a.m., or somewhat greater increases (but not greater concentrations) of precursor concentrations between approximately 10 a.m. and 1 p.m. than on weekdays. On the whole, however, the weekend precursor

concentration profiles resemble weekday profiles; they do not resemble the hypothetical weekend emission profile shown as Figure 2-4 of the CARB report.

As noted in the CARB report (Figure 2-2), chamber experiments support the idea that ozone production can be accelerated in a system that has reached a state of NO_x limitation by injecting fresh NO_x . However, the weekend effect occurs at VOC-limited sites, not NO_x -limited locations. Therefore, the relevance of the cited chamber experiments as an explanation of the weekend effect is not apparent.

Those aspects of the " NO_x -timing" hypothesis that have not been resolved by existing data appear to be amenable to reasonably straight-forward analyses using either photochemical box models or three-dimensional gridded models. The need for "Accurate, artifact free measurements of VOCs and NO_x in three dimensions" (Austin et al., 2000) may not be sufficiently pressing to warrant the expense of special field sampling.

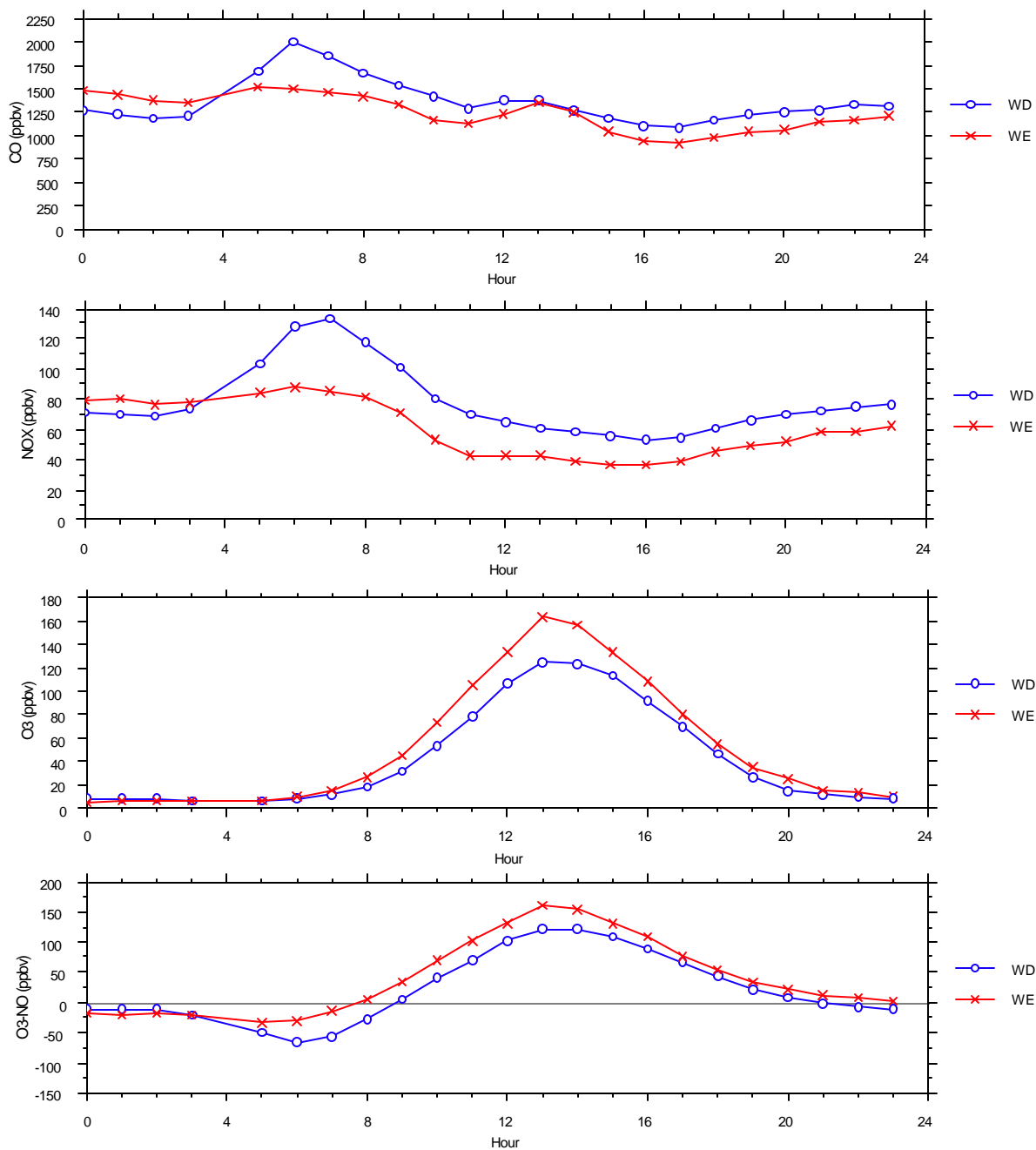


Figure 3. Diurnal concentration profiles for CO, NO_x, ozone, and O₃-NO at Azusa. The data are from 1995 through 1998 and are averages of the highest three ozone days on each day of the week each year (~ top 21 days per year, April through October).

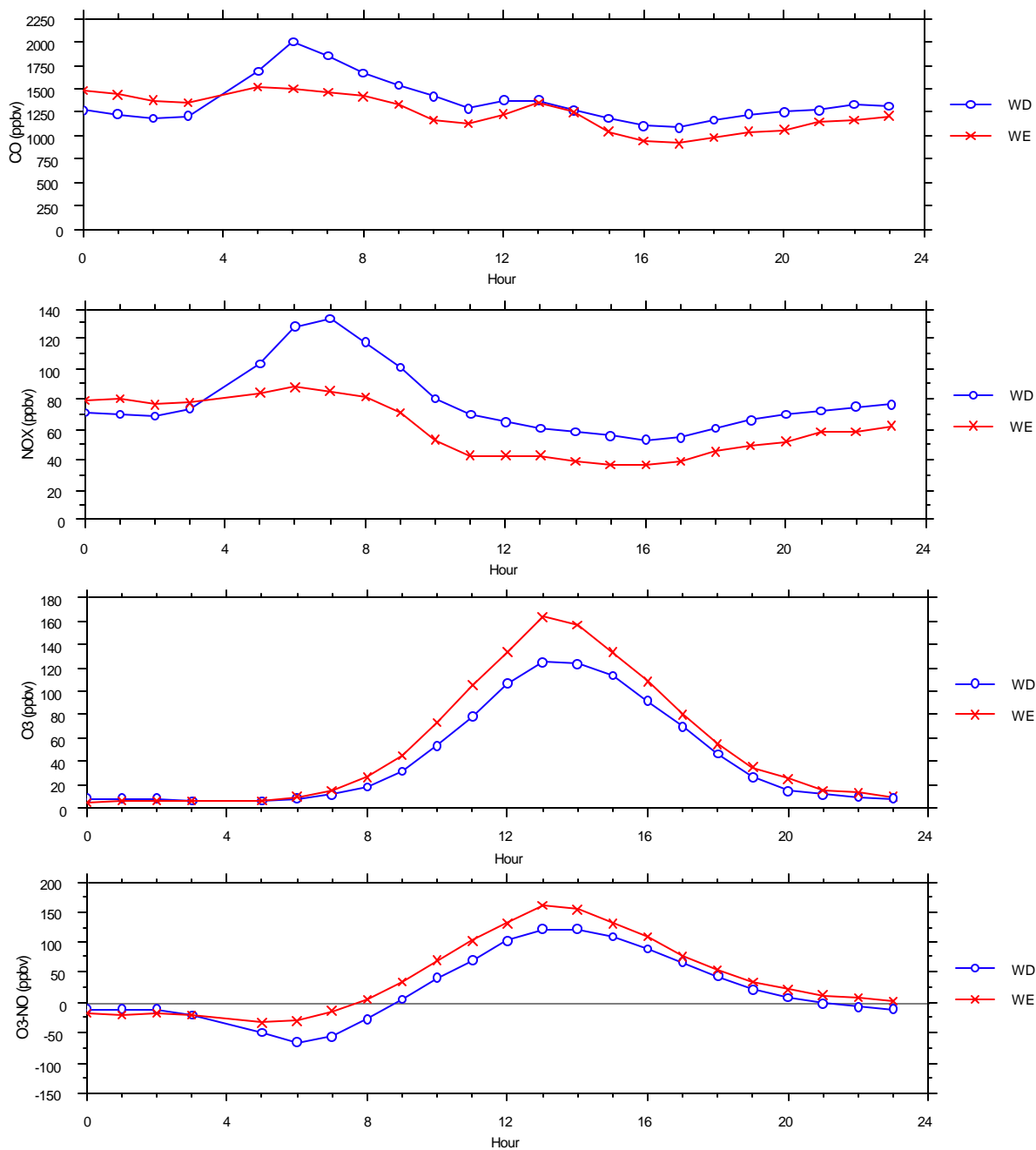


Figure 4. Diurnal concentration profiles for CO, NO_x, ozone, and O₃-NO at Pasadena. Data are from 1995 through 1998 and are averages of the highest three ozone days on each day of the week each year (~ top 21 days per year, April through October).

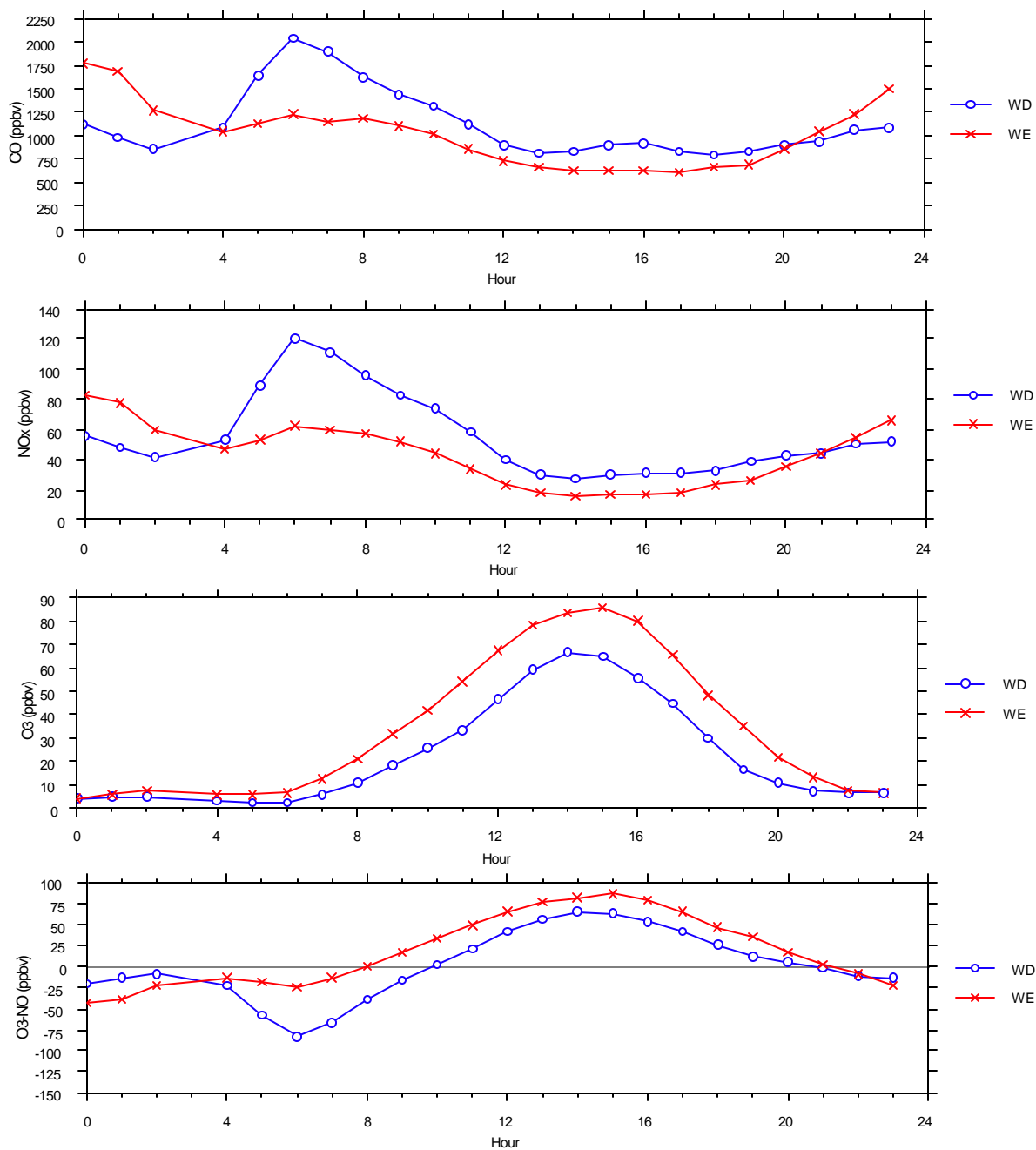


Figure 5. Diurnal concentration profiles for CO, NO_x, ozone, and O₃-NO at San Jose. Data are from 1995 through 1998 and are averages of the highest three ozone days on each day of the week each year (~ top 21 days per year, April through October).

As previously noted, the "Carryover aloft" hypothesis is in fact linked to the "NO_x reduction" hypothesis. The hypothesis states that reservoirs of higher concentrations of ozone aloft exist, but are titrated by fresh NO_x emissions as vertical mixing increases during weekday mornings; "On Saturday and Sunday, however, NO_x emissions are reduced substantially, ozone and radicals that carry over are not quenched, and they cause ozone measurements at the surface to be higher on weekends compared to weekdays."

Ample evidence supports the existence of higher concentrations of ozone aloft. As noted in the CARB report, during morning hours of the SCOS97 when ozone concentrations at surface sites were depleted, concentrations were often in the range of 40 to 80 ppbv at ~400 m to 4000 m agl; occasionally, concentrations of 140 ppbv or more were observed. During the 1987 Southern California Air Quality Study (SCAQS), aloft ozone concentrations exceeding 200 ppbv were recorded (Roberts and Main, 1992). Aircraft measurements recorded average aloft ozone concentrations in the range of 60 to 120 ppbv in the San Joaquin Valley and Bay Area during the 1990 San Joaquin Valley Air Quality Study (SJVAQS) (Blumenthal et al., 1997).

As noted in the CARB report (Austin et al., 2000), it is likely that air masses aloft are typically more aged than those at the surface, implying that further formation of ozone aloft may often be limited by the availability of NO_x. Analyses of surface and aloft measurements of NO_x and hydrocarbons collected at various locations in the San Francisco Bay Area and the San Joaquin Valley during the 1990 SJVAQS have provided evidence that aloft air masses are more aged than surface samples during early morning hours, and are more aged than afternoon aloft samples (Blumenthal et al., 1997). These conclusions were supported by comparing ratios of VOC/NO_x, xylenes/benzene, and toluene/benzene (xylenes and toluene react more rapidly than benzene, so departures of those ratios from the ratios characteristic of fresh emissions provides an indication of aging). Data from other locations (see Figure 6) show that situations occur where early morning surface layers have low concentrations of ozone, depleted by reaction with fresh NO_x emissions, whereas NO_x levels in layers aloft are low and ozone concentrations have reached the maximum levels possible without further input of fresh emissions. In the

examples shown, ozone formation remained VOC-limited throughout the following daytime hours at the urban locations.

Many locations showing aged air aloft nonetheless exhibit same-day surface concentrations of ozone and precursor species that are indicative of VOC limitation. Specific cases must be studied carefully using modeling and a variety of data analyses to establish the probable consequences of various levels and combinations of VOC or NO_x emission reductions.

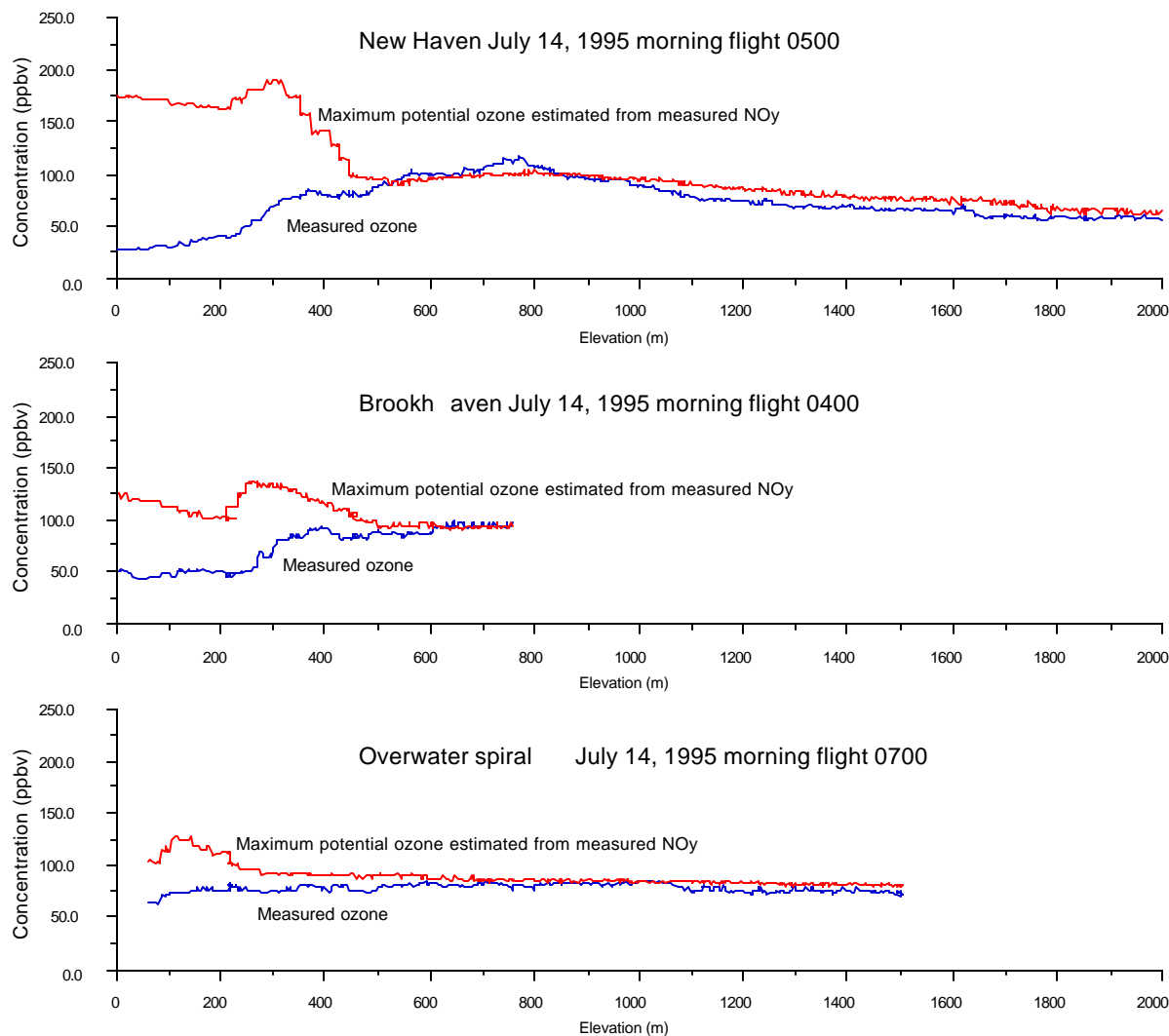


Figure 6. Aloft ozone concentrations on the morning of July 14, 1995 at three aircraft sampling locations during the NARSTO-Northeast study. The maximum potential ozone concentrations were predicted using the method of Blanchard et al. (1999). Source: Blanchard (1998).

The CARB report concludes that each of the three hypotheses discussed here is plausible, but none is proven and all may play some role. However, the CARB report and all other studies found considerable evidence to support the NO_x-reduction hypothesis, and that hypothesis is consistent with expectations derived from theory and from modeling studies. Also, sufficient evidence exists to show that aloft ozone concentrations exceed surface concentrations at many times and places, and do contribute to ground-level ozone values as vertical mixing occurs during the day. In the next section, control implications are considered. Indeed, what is needed is not further testing of these hypotheses. Rather, the primary need is to delineate control strategies that are effective at all times and places, including areas that are VOC-limited, areas that are NO_x limited, and areas dominated by transported ozone.

What are the Implications for Ozone Control Strategies?

Two of the principal conclusions of the CARB report pertain directly to ozone control strategies:

"Conclusion #2: A combination of VOC and NO_x reductions has been highly successful at reducing ambient ozone levels on all days of the week everywhere in the basin for more than 20 years in the South Coast Air Basin. Nevertheless, the ozone weekend effect occurs throughout the SoCAB.

Conclusions #3: The ozone weekend effect does not invalidate NO_x reductions as an important ozone control strategy. In addition, NO_x reductions are almost certainly beneficial in reducing concentrations of some other pollutants, such as, PM₁₀ nitrate, nitrogen dioxide, and PAN."

These conclusions may be better understood in light of the findings of the recently released NARSTO ozone assessment report (Chameides et al., 2000):

"A synthesis of results from field studies and model simulations ... suggests general rules for optimizing an O₃ abatement strategy. These include:

"For O₃ abatement programs focused on the urban core ... a VOC-based strategy will be most

effective. An important exception to this rule is in urban areas where natural VOC concentrations are large. In these cases, a NO_x-based strategy may be required even though the chemistry is VOC-limited ... Other possible exceptions include cases in which most of the O₃ in the urban core is transported from upwind, or cases where 'recirculation' of aged local pollution contributes significantly to O₃ in the urban core.”

"For O₃ abatement programs focused on regional air quality, a NO_x -based strategy will probably be most effective.”

"O₃ abatement strategies focused on lowering peak O₃ concentrations in and around urban areas present the most complex situation. ... Scenario 1: An urban O₃ episode with significant advection of polluted air parcels from the urban-core source region to suburban and outlying rural areas with significantly lower pollutant emissions ... likely will require both VOC and NO_x controls. Scenario 2: An urban O₃ episode with strong stagnation in an area with dispersed pollutant sources throughout the suburban as well as urban core ... VOC-limitation applies throughout the area, even to the peak O₃ concentrations, and thus mitigation will require VOC controls.”

In California, the full range of situations identified in the NARSTO assessment guidance exists. The spatial variations of the weekend effect appear to be one indication of this variety, as suggested, for example, by Figures 1 and 2. The urbanized central portions of the South Coast Air Basin and the San Francisco Bay Area are prime examples of VOC-limited, urban-core areas where ozone episodes are driven by stagnation and are much less influenced by transport from upwind, and where biogenic VOC emissions are not dominant. The NARSTO guidance identifies such areas as candidates for VOC-focused emission-reduction strategies. The weekend effect is particularly prominent at sites within these regions, and provides empirical support for the NARSTO guidance.

Some other areas within California are likely to benefit from NO_x-focused control strategies.

As indicated in the NARSTO guidance, such areas might include many of the national parks and other Class I areas within California, such as Joshua Tree, Sequoia, and Yosemite national parks. Presently, ozone concentrations within such locations are lower on weekends than on weekdays (Figures 1 and 2). Violations of the federal 1-hour ozone standard occur in Joshua Tree National Park.

Because of the range of conditions occurring throughout California, statewide emission-reduction strategies must include both VOC and NO_x. Locally, however, ozone formation is either limited by VOC or by NO_x, and the most effective local control strategies will target the limiting precursor in each area. As reported in Austin et al. (2000), ozone concentrations have trended strongly downward in the South Coast Air Basin since 1980, so the control strategies that have been employed have indeed been successful. However, the data cannot show that those strategies have been optimal, as no alternatives to the historical emission control program exist for comparison. Nonetheless, several observations are possible.

Unlike the difference between weekdays and weekends, the NO_x reductions occurring over the period 1980 through 1998 were accompanied by even stronger VOC reductions; thus, ozone concentrations declined throughout the South Coast Basin and the Bay Area, even at sites that exhibit a weekend effect. Thus, future emission controls focusing on VOC reductions, combined with lesser reductions of NO_x, need not increase ozone concentrations in the South Coast Air Basin or the San Francisco Bay Area, though the weekend effect warns that future controls focusing primarily on NO_x reductions might. But slower rates of progress may occur in the urban areas than would be the case if only VOC emissions were reduced. Aggressive VOC control measures applied to stationary sources in the past have reduced the proportions of total emissions attributable to stationary sources, so that at present both VOC and NO_x emissions are dominated by mobile sources in the Los Angeles and San Francisco Bay areas. Future control efforts, such as those listed in the Bay Area 2000 Clean Air Plan, consist of approximately equal reductions of VOC and NO_x emissions.

Since NO_x reductions are likely effective for reducing ozone levels regionally, statewide

requirements (e.g., motor vehicle NO_x-emission standards) play an important role in the overall approach to ozone management. Moreover, ozone reductions may also occur as a result of local reductions of NO_x emissions within areas where ozone formation is NO_x-limited. In contrast, reductions of NO_x emissions within areas that are strongly VOC limited are unlikely to provide regional benefits, and are likely to aggravate ozone concentrations locally. It is likely that imposition of local NO_x controls on sources within areas presently experiencing a weekend effect may enhance ozone formation rates, or, may partially or fully offset further VOC controls.

The CARB report (Austin et al., 2000) summarizes several relevant findings from earlier studies. In subregions of the South Coast Air Basin,

- "On a daily basis, maximum ozone concentrations in each sub-region related more strongly to morning NO_x concentrations locally than to NO_x concentrations in any other sub-region. This was true of 'downwind' or 'receptor' sub-regions as well as 'upwind' or 'source' sub-regions.
- Surface carryover of NO_x was not an important factor affecting day-of-the-week differences in ozone.
- Daily maximum ozone concentrations, characterized by the average of the highest 10 daily maxima each year, showed the greatest decrease in the areas with the greatest percentage decrease in early morning NO_x concentrations."

Thus, where lowering NO_x emissions reduces ozone concentrations, local emission reductions appear most effective. However, confirmation of the importance of local NO_x emissions on ozone formation in NO_x-limited areas is needed using an integrated analysis of three-dimensional modeling studies and ambient measurements. The SCOS97 and the ongoing Central California Ozone Study (CCOS) provide suitable databases for modeling and analysis. Modeling studies that employ process analysis are capable of revealing the relative contributions of locally-generated and transported ozone, as well as the effects of precursors emitted in one area on ozone formation in another. Process analysis has been incorporated into the models currently being used to study ozone formation in central California.

Maps showing where the weekend effect occurs (Figures 1 and 2) reveal a particularly

interesting effect for further study. Higher weekend ozone concentrations occur in the San Francisco Bay Area and in the South Coast Air Basin. Yet, areas located east of these two air basins, and that are thought to receive pollutants from them, show lower weekend ozone concentrations. Indeed, many studies have documented transport of ozone from the South Coast Air Basin into the Mojave Desert. Therefore, local ozone formation in the downwind areas (e.g., Mojave Desert, east of Sacramento) either must dominate ozone concentrations, or it must be sufficiently reduced on weekends to compensate for the higher weekend ozone concentrations occurring upwind. This observation is consistent with other evidence suggesting that precursor changes occurring in the Bay Area and the SoCAB may be ineffective in reducing ozone formation in downwind areas. That is, strategies that most rapidly reduce ozone concentrations within the Bay Area and the SoCAB would benefit downwind areas by reducing the levels of transported ozone. NO_x reductions within NO_x -limited areas, such as east of Sacramento, should be effective in reducing ozone concentrations in those areas; NO_x reductions made upwind in VOC-limited areas may not reduce ozone formation downwind, and may lessen progress in reducing downwind ozone concentrations by slowing rates of ozone reductions in the upwind areas. These observations are testable using three-dimensional model studies with appropriate databases and model evaluation.

An additional area meriting further investigation is the effect of VOC and NO_x reductions on aerosol nitrate formation. Aerosol nitrate derives from emissions of nitrogen oxides, but in a highly nonlinear manner. The formation of aerosol nitrate via reaction of nitric acid and ammonia may be limited by the concentrations of either reactant, with the less abundant reacting species being the limiting factor. However, the amount of aerosol nitrate formed depends upon temperature, humidity, and concentrations of other species, especially sulfate. Additional reactions of nitric acid with sea-salt aerosol also yield particulate nitrate in some coastal areas. Blanchard et al. (2000) concluded that aerosol and gas-phase measurements from one long-term and two short-term studies in California showed that aerosol nitrate formation generally was not limited by the availability of ammonia. Kumar et al. (1998) derived a similar conclusion for the San Joaquin Valley. However, like ozone, the rate of formation of nitric acid may be limited either by radicals or by NO_x . Therefore, in some situations,

aerosol nitrate formation may be more effectively reduced through reductions of VOC than NO_x emissions (Pun and Seigneur, 1999). More specifically, existing work suggests that VOC reductions may reduce the rate of aerosol nitrate formation especially in areas where ozone formation is VOC limited. Additional research efforts should be directed to this topic.

What Research Efforts are Needed?

The CARB report concludes that "Accurate, artifact free measurements of VOCs and NO_x in three dimensions are needed to assess the contributions of the "NO_x-reduction" hypothesis, the "NO_x-timing" hypothesis, and the "Carryover aloft" hypothesis." Yet, regardless of the relative contributions of each process to the overall weekend effect, ample scientific evidence exists to indicate that the range of conditions in California requires geographically-focused reductions of VOC and NO_x emissions, with emphasis on VOC reductions in areas known to be strongly VOC-limited (e.g., most of the San Francisco Bay Area, South Coast Air Basin, and San Diego Air Basin) and NO_x reductions where ozone is NO_x-limited. Since the latter require statewide strategies in some cases (e.g., motor vehicles), careful consideration should be given to the balance of VOC and NO_x controls imposed within the coastal metropolitan areas. Regardless of the exact contributions of each plausible cause to the overall weekend effect, the undisputed magnitudes of the increased weekend ozone concentrations within the San Francisco Bay Area, South Coast Air Basin, San Diego Air Basin, and some urban locations within the Central Valley indicate that control strategies in which NO_x emission reductions exceed VOC emission reductions are likely to aggravate ozone concentrations in those areas. The weekend effect provides a clear test case.

Ongoing field studies are already in place to provide further data for understanding the weekend effect (Fujita et al., 2000). Thus, a more productive use of resources would be to focus on evaluating geographically-targeted ozone control strategies, rather than on testing hypotheses of the weekend effect. Further analysis of data from the SCOS97 and CCOS projects, along with modeling studies, should be pursued. An additional topic meriting further investigation is the effect of VOC and NO_x reductions on aerosol nitrate formation. This research need was previously identified by analyses

conducted under the Central California Regional Particulate Air Quality Study (CRPAQS) and should be investigated further using data from the Central California Regional Particulate Air Quality Study, along with modeling studies.

Conclusion

Recent studies all concur in concluding that a weekend effect occurs in California throughout much of the South Coast Air Basin (SoCAB), the San Francisco Bay Area, and the San Diego metropolitan area; it also occurs at monitoring sites within other urban centers, including Sacramento, Stockton, and Fresno (Austin et al., 2000; Blanchard and Tanenbaum, 2000; Fujita et al, 2000; Altshuler et al., 1995). These same studies also consistently concur in concluding that ambient concentrations of ozone precursors are lower during the daytime on weekends than on weekdays throughout most of eight air basins in California (San Francisco Bay area, Sacramento Valley, San Joaquin Valley, South Coast, South Central Coast, San Diego, Mojave Desert, and Salton Sea). The magnitudes of the differences vary from hour to hour, but at most monitoring sites NO_x concentrations are reduced more than VOC concentrations on weekends.

Of six candidate proposed explanations of the weekend effect, a recent CARB report (Austin et al., 2000) concluded that presently available data were sufficient to show that two were not plausible. The two implausible hypotheses were "carryover near the ground" and "increased weekend emissions", both of which are refuted by ambient measurements showing lower concentrations of ozone precursors during daytime weekend hours than during corresponding weekday hours. Three hypotheses were considered plausible, but not proven: " NO_x reduction", " NO_x timing", and "carryover aloft." Finally, a "soot and sunlight" hypothesis was considered theoretically plausible, but lacking in either supporting or refuting data.

A key commonality of the three plausible hypotheses with supporting data is that all involve the effects of NO_x on ozone; the hypotheses are in fact tightly linked. They differ in the degree of emphasis placed on the effects of mid-day emissions of NO_x , and the relative contributions of carryover ozone to

peak ozone concentrations. Review of the full range of available studies, including Austin et al. (2000), Fujita et al. (2000), Blanchard and Fairley (1999), and Blanchard and Tanenbaum (2000), shows that all concur in describing the effects of lowered NO_x levels on ozone formation at urban-center sites: NO concentrations fall to low levels earlier, and ozone formation begins earlier, on weekends than on weekdays at sites in the South Coast Air Basin (Fujita et al., 2000); "Ozone concentrations at many sites (not including far downwind sites) tend to increase earlier in the day on weekends compared to weekdays." (Austin et al., 2000). These effects are expected, based upon a large body of historical work, at locations where ozone formation is radical (VOC)-limited: fresh NO emissions lower ozone concentrations by virtue of the reaction of NO with ozone, and they reduce rates of ozone formation by lowering radical concentrations.

Substantial agreement also exists among both the recent studies and historical work (see e.g., Chameides et al., 2000) in identifying where ozone formation is limited by radicals (VOC) and where it is limited by NO_x in California. The spatial patterns of the weekend effect match the spatial patterns delineating where ozone formation is VOC limited in both southern and northern California: the weekend effect occurs at locations where ozone formation is VOC-limited.

Regardless of the relative contributions of each plausible process to the overall weekend effect, ample scientific evidence exists to indicate that the range of conditions in California requires geographically-focused reductions of VOC and NO_x emissions, with emphasis on VOC reductions in areas known to be strongly VOC-limited (e.g., most of the San Francisco Bay Area, South Coast Air Basin, and San Diego Air Basin) and NO_x reductions where ozone is NO_x-limited. The latter involve regional ozone reductions, and require statewide control strategies in some cases (e.g., motor vehicles). The weekend effect indicates that careful consideration should be given to the balance of VOC and NO_x controls imposed within the coastal metropolitan areas. The undisputed magnitudes of the increased weekend ozone concentrations within the San Francisco Bay Area, South Coast Air Basin, San Diego Air Basin, and some urban locations within the Central Valley indicate that control strategies in which NO_x emission reductions exceed VOC emission reductions are likely to aggravate ozone

concentrations in those areas. The weekend effect provides a clear test case.

Ongoing field studies are already in place to provide further data for understanding the weekend effect (Fujita et al., 2000). The need for an additional comprehensive and extended field program to further distinguish among the plausible explanations of the weekend effect is not apparent. A more productive use of resources would be to focus on evaluating geographically-targeted ozone control strategies, rather than on testing hypotheses of the weekend effect. Further analysis of data from the 1997 Southern California Ozone Study (SCOS97) and the ongoing Central California Ozone Study (CCOS) projects, along with modeling studies, should be pursued. An additional topic meriting further investigation is the effect of VOC and NO_x reductions on aerosol nitrate formation. Existing studies indicate that aerosol ammonium-nitrate formation in California is typically not limited by the availability of ammonia. However, existing work from the San Joaquin Valley Integrated Monitoring Study of 1995 (IMS95) also suggests that VOC reductions may reduce the rate of aerosol nitrate formation more effectively than NO_x reductions in areas where ozone formation is VOC limited. This topic should be investigated through analyses of data from the Central California Regional Particulate Air Quality Study (CRPAQS), along with modeling studies.

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